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The crystal structure of δ-$Al(OH)_3$: Neutron diffraction measurements and ab initio calculations

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Abstract

δ-$Al(OD)_3$ powders were synthesized from $Al(OD)_3$ bayerite at 4 GPa and 523 K using a cubic press apparatus. Neutron powder diffraction analyses of δ-$Al(OD)_3$ at ambient conditions revealed that the crystals are orthorhombic with space group $P2_12_12_1$, not *Pnma* as reported previously based on X-ray diffraction data. The $P2_12_12_1$ δ-$Al(OH)_3$ structure contains seven independent atoms in the asymmetric unit, including one Al, three O, and three H atoms. The initial lattice parameters and the atomic positions of both Al and O were taken from previous X-ray structural analyses of the *Pnma* structure, while the positions of H were determined in the present study using ab initio calculations to (1) give the least energy among trial structural models for $P2_12_12_1$ δ-$Al(OH)_3$, (2) accurately reproduce the measured lattice parameters of δ-$Al(OD)_3$, and (3) show reasonable energetic relations between the $Al(OH)_3$ polymorphs; namely, gibbsite is stable at ambient pressure, δ-$Al(OH)_3$ has the lowest enthalpy at pressure greater than 1.1 GPa, and both bayerite and η-$Al(OH)_3$ are metastable over the entire pressure range. Furthermore, we found that the structure of δ-$Al(OH)_3$ obtained from ab initio calculations is in good agreement with that derived from a Rietveld refinement of δ-$Al(OD)_3$, based on the present powder neutron diffraction data. The δ-$Al(OH)_3$ structure possesses one relatively long and two short O-H···O hydrogen bonds. Ab initio calculations also reveal that δ-$Al(OH)_3$ with space group $P2_12_12_1$ transforms to another high-pressure polymorph with space group *Pnma* at around 67 GPa, and that the two short hydrogen bonds in δ-$Al(OH)_3$ become both symmetric through the $P2_12_12_1$ to *Pnma* transformation, in which the protons are located at the midpoints of the O···O hydrogen bonds.

Keywords: $Al(OH)_3$, high pressure, neutron diffraction, ab initio calculations, symmetrical hydrogen bond